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1. REPORT DATE (DD-MM-YYYY)		2. REPORT DATE June 25, 2001		3. DATES COVERED (From - To) Interim Report							
4. TITLE AND SUBTITLE Synthesis and Electrochemical Properties of High Surface Area Sol-Gel Materials				5a. CONTRACT NUMBER 5b. GRANT NUMBER N00014-93-1-0245 5c. PROGRAM ELEMENT NUMBER PR No: 01PR0086-00							
6. AUTHOR(S) Jeffrey S. Sakamoto, Winny Dong and Bruce Dunn				5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER							
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Bruce S. Dunn Department of Materials Science and Engineering University of California, Los Angeles Los Angeles, CA 90095				8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report #16							
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217				10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSORING/MONITORING AGENCY REPORT NUMBER							
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13. SUPPLEMENTARY NOTES Submitted for publication in: <i>Proceedings of the Workshop on Interfaces, Phenomena and Nanostructures in Lithium Batteries</i>											
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15. SUBJECT TERMS vanadium oxide, aerogel, electrochemical properties, composite electrodes											
16. SECURITY CLASSIFICATION OF: <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%; padding: 2px;">a. REPORT</td> <td style="width: 33%; padding: 2px;">b. ABSTRACT</td> <td style="width: 33%; padding: 2px;">c. THIS PAGE</td> </tr> <tr> <td style="text-align: center; padding: 2px;">U</td> <td style="text-align: center; padding: 2px;">U</td> <td style="text-align: center; padding: 2px;">U</td> </tr> </table>			a. REPORT	b. ABSTRACT	c. THIS PAGE	U	U	U	17. LIMITATION OF ABSTRACT		18. NUMBER OF PAGES 11
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20010705 068

OFFICE OF NAVAL RESEARCH

GRANT: N00014-93-1-0245
R&T Code: 4133041
PR Number: 01PR00860-00

Dr. Richard Carlin

Technical Report #16

**Synthesis and Electrochemical Properties of High Surface Area
Sol-Gel Materials**

By

Jeffrey S. Sakamoto, Winny Dong and Bruce Dunn

Submitted for publication in:
*Proceedings of the Workshop on Interfaces, Phenomena and
Nanostructures in Lithium Batteries*

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June 25, 2001

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SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF HIGH SURFACE AREA SOL-GEL MATERIALS

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ABSTRACT

The sol-gel process enables one to create electrochemical materials with designed chemistry and microstructure. By controlling the chemistry of the process, one can prepare amorphous oxides or metastable phases with tailored morphology. One direction for this approach has been to synthesize high surface area transition metal oxide aerogels. The continuous microporous and mesoporous volume provides both molecular accessibility and rapid mass transport via diffusion. In this paper we review our recent work directed at characterizing the fundamental electrochemical properties of vanadium oxide aerogels. Using a sticky-carbon electrode, we find that vanadium oxide aerogels combine both capacitor and battery-like behavior. Another direction for our work has involved the use of carbon nanotubes as the conducting network in a reversible electrode. These electrodes exhibit enhanced lithium capacity, especially at high rates, as compared to conventional composite electrodes.

INTRODUCTION

The sol-gel process offers a convenient synthetic route for creating electrochemical materials with very different properties as compared to traditional solid-state chemical methods. By controlling the chemistry of the process, one can prepare amorphous and metastable oxide phases with tailored microstructure; from highly porous, high surface area aerogels to fully dense materials.¹

The present paper concerns one of the interesting directions for the sol-gel process, that of synthesizing high surface area transition metal oxide aerogels. Aerogels represent a nanoscale, mesoporous material in which both the solid and mesoporous volumes are continuous. The ample porosity provides both molecular accessibility and rapid mass transport via diffusion and for these reasons aerogels have been investigated for heterogeneous catalytic materials for over 50 years. One would expect that this morphology would also be desirable for electrochemical reactions, facilitating electrolyte penetration into the entire aerogel particle through the mesoporous network. Although only a few aerogel systems have been investigated as electrochemical materials, rather good electrochemical behavior has been reported.² The vanadium oxide system is particularly interesting in that the lithium capacity for the aerogels is better than that of V_2O_5 xerogels or crystalline V_2O_5 .³ Comparisons to xerogels are especially intriguing

since the differences between *aerogels* and *xerogels* are morphological (primarily porosity and surface area) and not chemical; the materials differ only by the manner in which they are dried.² The aerogel materials offer considerable promise for battery applications with a specific lithium capacity in excess of 300 mAh/g at a C/4 discharge rate.⁴

The present paper considers two different types of experiments which relate to the nanoscale morphology of V_2O_5 aerogels. First, we report on experiments concerning fundamental electrochemical properties of the aerogel. In this work a sticky-carbon electrode was used to avoid modifying the unique solid-pore nanostructure of the aerogel. In the second part of this paper we describe our efforts at incorporating carbon nanotubes as the conducting network in a reversible lithium electrode. Because the carbon nanotubes are of the same dimensional scale as the vanadium oxide ribbons, the nanocomposite electrode effectively retains the mesoporous morphology of the aerogel.

EXPERIMENTAL

Materials Synthesis

The vanadium oxide aerogels were prepared using supercritical drying (scd) and ambient drying ('ambigel') methods. For both methods, an alkoxide precursor, vanadyl triisopropoxide, was hydrolyzed in a water-acetone mixture. Details for preparing scd and ambigels of vanadium oxide were reported previously.^{5,6} The latter approach involved the use of solvent exchange with a non-polar solvent. The combination of scd and ambigel methods enabled us to prepare mesoporous vanadium oxide materials with a range of surface areas, porosities and pore volumes as shown in Table 1. When no solvent exchange occurs and the wet gel is dried in ambient, the resulting material is a xerogel.

Table I. Surface area and porosity data for vanadium oxide aerogel

Drying liquid	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Specific Capacitance (F/g)
Acetone (xerogel)	<10	<0.01	620
cyclohexane	155	0.87	2150
heptane	200	0.60	1660
hexane	165	0.40	1240
pentane	185	0.48	960
supercritical CO ₂	280	0.50	1300

Nanocomposites of vanadium oxide aerogel with single-walled carbon nanotubes (SWNT) were prepared by integrating the nanotubes as part of the sol-gel chemistry. The key feature in preparing the V_2O_5 -SWNT nanocomposite cathodes was to use a suspension of SWNT's as the source of diluting solvent (acetone) in preparing the gel. The SWNT's were received in toluene that was gradually replaced with acetone. Although some agglomeration of SWNT's occurred upon adding acetone, the SWNT's

remained suspended and did not sediment. This suspension was then combined with the requisite amounts of vanadium alkoxide precursor and water to produce a wet gel. The gelled samples were washed repeatedly in anhydrous acetone and then solvent exchanged with cyclohexane. The cyclohexane was evaporated under ambient conditions to produce the final nanocomposite.

Electrochemical Measurements

Electrochemical properties for the two types of V_2O_5 aerogels were determined using sticky-carbon electrodes.^{7,8} This method avoids the particle agglomeration which occurs in preparing conventional electrodes and would alter the pore-solid nanoscale morphology of the aerogel. The sticky-carbon electrode provides a sticky surface for adhering a quantitative amount of aerogel powder, while exposing the submicron particles to the electrolyte and providing good electrical contact to each particle.

The nanocomposite electrodes were prepared by mixing the V_2O_5 -SWNT powder with PVDF in cyclohexane to form a slurry which was then applied to a stainless steel mesh. The electrode material was dried under vacuum at 240°C prior to measurement. For comparison, standard electrodes were prepared using Ketjen Black (KJB) as the conductive additive. The wt% of KJB mixed with the vanadium oxide ambigel was comparable to that of the SWNT component in the nanocomposite. The same slurry and cathode preparation method was used as described for the nanocomposite.

The electrochemical measurements for both types of experiments were carried out in an Ar-filled glove box using a conventional three-electrode cell with lithium foil reference and counter electrodes. The working electrode was either (a) the sticky-carbon electrode by itself, (b) the sticky-carbon electrode modified with the V_2O_5 aerogel powder, (c) the V_2O_5 -SWNT electrode or (d) the V_2O_5 -KJB electrode. The electrolyte was 1.0 M lithium perchlorate in anhydrous propylene carbonate. In some experiments involving (a) and (b), an electrolyte of 0.1 M tetrabutylammonium perchlorate (TBAP) in propylene carbonate was utilized.

RESULTS AND DISCUSSION

Sticky-Carbon Electrode Studies⁸

The voltammetric responses for the aerogel immobilized on the sticky-carbon electrode are shown in Figure 1 for the $LiClO_4/PC$ electrolyte. The faradaic features are broad and capacitive and the intercalation peaks appear superimposed upon the capacitive response (Fig. 1a). The background from the sticky carbon electrode is negligible. As one goes to higher scan rates, the aerogel responds as a capacitor. This capacitive response is substantially different from that which is obtained for the same V_2O_5 aerogel when it is prepared in a conventional composite electrode structure (i.e., with KJB as the conductive additive). In this case, the electrode displays the characteristic intercalation behavior for sol-gel derived V_2O_5 materials (Fig. 1b).

Table 1 lists specific capacitances, multipoint BET surface areas and pore volumes for the various samples investigated in this work. Depending upon the details of the aerogel

drying process, the specific capacitance values range from 960 F/g to over 2000 F/g. The largest specific capacitance was obtained using cyclohexane as the drying solvent (2150 F/g) which corresponds to nearly 1500 $\mu\text{F}/\text{cm}^2$. Interestingly, this material does not exhibit the largest surface area of all the aerogels, but does possess the greatest pore volume.

Electrochemical measurements using the TBAP electrolyte indicate a significantly lower capacitance (Figure 2). In this case, the response for the aerogel immobilized on the sticky carbon is greater than that of the sticky carbon background, but significantly less than that obtained in the Li^+ electrolyte. The capacitance per unit area for this sample, 50 $\mu\text{F}/\text{cm}^2$, is consistent with what one obtains for surface-area-normalized double-layer capacitance at smooth electrodes. The interesting part of this experiment is that it represents a control; with the larger diameter of the TBA^+ ($\sim 9 \text{ \AA}$), only surface adsorption of the ion is expected. Thus, the substantially greater voltammetric charge that occurs using the Li^+ electrolyte (460 $\mu\text{F}/\text{cm}^2$) shows the importance of ion penetration in the V_2O_5 aerogel structure.

The data in Table 1 point out a subtle influence of aerogel morphology on the electrochemical properties. It is evident from the Table that the specific capacitance does not correlate with the BET surface area for the V_2O_5 aerogels. Instead, there is a fairly linear trend between specific capacitance and pore volume for the various aerogel samples.⁸ This behavior indicates the importance of pore architecture. Supercritically dried aerogels have high surface areas but moderate pore volume because there are many nano-sized pores in the sample with diameters less than 5 nm. These small pores may not be readily accessible to the ions and solvent and, in that case, their contribution to the overall sample capacitance will be nominal. In contrast, samples dried with a low surface tension solvent at ambient pressure tend to have larger pores, in the range of 10 to 30 nm,⁶ leading to correspondingly greater pore volume. In this size range, electrolyte penetration is not likely to be impeded.

The sticky-carbon electrode studies show that the inherent electrochemical properties of the aerogel are entirely different from those obtained using a traditional composite electrode. In Li^+ electrolytes, the sticky-carbon voltammograms are dominated by a capacitive response and the magnitude of the voltammetric charge indicates pseudocapacitive behavior. The fact that pseudocapacitance is observed rather than double layer capacitance is not surprising in view of the similarities between intercalation and pseudocapacitance.⁹ It is evident that ion incorporation remains an important consideration since double-layer capacitive behavior occurs in experiments using the larger TBAP ion.

The results with the sticky-carbon electrode underscore the importance of measuring the electrochemical properties of the aerogel under conditions that do not compromise its networked mesoporous architecture. In the present experiments, electron, ion and solvent transport are enhanced as compared to traditional electrode structures. The resulting behavior displays a combination of battery-like ion incorporation and capacitor-like response. We have suggested that the origin of this behavior must somehow be influenced by the fact that the high surface area of the aerogels amplifies surface

phenomena.² Surface defects that are not very prominent in bulk materials can now influence, if not dominate, electrochemical properties.

Vanadium Oxide Aerogel-Carbon Nanotube Composite Electrodes

The microstructure of the V_2O_5 -SWNT nanocomposite is shown in Figure 3. There is intimate contact between the two phases as several aerogel fibers are intertwined with several SWNT's. The latter are characterized by strongly absorbing regions that are probably the metal nanoparticles used as catalysts during SWNT synthesis. This and other TEM images confirm that the resulting microstructure is the one that was intended. That is, the conductive additive, i.e. carbon nanotubes, establishes extensive contact with the vanadium oxide aerogel at the nanometer dimensional level, and electrolyte access is not likely to be hindered by the presence of the SWNT phase.

BET measurements were used to evaluate pore size, pore volume and surface area for the V_2O_5 aerogel as well as the V_2O_5 -SWNT and V_2O_5 -KJB composite electrodes. Table 2 shows that the addition of the conductive additive reduces the surface area and pore volume as compared to the pure aerogel. It is important to note that both composites exhibit similar pore volumes, which is an important consideration for electrolyte access. The addition of SWNT has less of an effect on surface area as compared to the KJB.

Table 2. Morphology of vanadium oxide aerogel and aerogel composites with conductive additives SWNT and KJB.

Sample	BET surface area (m^2/g)	Avg. Pore Diameter (Angstroms)	Pore volume (cm^3/g)
V_2O_5 aerogel	150	300	0.97
V_2O_5 -KJB (17 wt%) Composite	73	310	0.59
V_2O_5 -SWNT (5 wt %) Composite	150	205	0.77
V_2O_5 -SWNT (17 wt%) Composite	120	190	0.59

Cyclic voltammetry was used to analyze the active voltage range for both a SWNT electrode and the V_2O_5 -SWNT (17 wt%) nanocomposite electrode (Figure 4). Well defined reduction and oxidation peaks occur at 2.4 and 2.8 Volts, respectively, for the V_2O_5 -SWNT electrode while the current response over the entire range is negligible for the SWNT electrode. This result shows that SWNT's are relatively inactive from 4 to 1.5 Volts and do not contribute to the capacity of the V_2O_5 -SWNT composite electrodes. This behavior is consistent with reported literature indicating that lithium reacts with SWNT's at voltages less than 1.5 V.¹⁰

One issue we wanted to examine was the influence of electrode morphology on rate capability. In these experiments, the specific discharge capacity (mAh/g) was measured

as a function of specific current (mA/g) for two different V_2O_5 -SWNT nanocomposite electrodes (9 and 17 wt%) and compared to a traditional electrode (V_2O_5 -KJB) which had an equivalent amount of conductive additive (17 wt%). The data (Figure 5) display an interesting trend. At relatively low specific current (112 mA/g) the specific capacities for the different electrodes are approximately the same. The kinetic limitations are insignificant at this discharge rate, and the rather high capacity values for V_2O_5 aerogels (~ 450 mAh/g) are obtainable. The specific capacities at 112 mA/g agree reasonably well with the ones reported by Coustier et al.⁴ At slightly higher specific currents (560 mA/g), differences begin to appear. The specific capacity of the V_2O_5 -SWNT (17wt%) composite decreases slightly (418 mAh/g) while the V_2O_5 -SWNT (9wt%) and the 17wt% KJB cathode are below 400 mAh/g. As the specific current is increased even further, i.e. > 560 mA/g, the specific capacities for both the 9 and 17 wt% V_2O_5 -SWNT cathodes are significantly greater than the 17wt% KJB cathode. At 2800 mA/g the specific capacity for the V_2O_5 -SWNT (17wt%) nanocomposite cathode is approximately twice as large as the V_2O_5 -KJB (17wt%) traditional electrode.

The results shown here are quite interesting in that the basic morphology for each type of electrode was comparable. That is, as shown in Table 2, the pore volume is not substantially different for the various electrodes and, electrolyte access is expected to be similar. It would seem then that the low electrical resistance arising from the intimate contact between the nanotubes and the vanadium oxide fibers must be an important consideration for achieving high rate capability. At this time we have made only qualitative measurements of the electrical resistance of the electrodes. It is apparent that electrodes prepared with carbon nanotubes as the conductive network exhibit substantially lower resistivities (by about a factor of 4) compared to electrodes containing the same weight fraction of the KJB additive. It is not surprising, therefore, that the performance of the cathodes with a lesser amount of SWNT (i.e., 9 wt %) is comparable or better than the traditional electrodes containing nearly twice as much KJB (17 wt %).

Galvanostatic cycling experiments for the V_2O_5 -SWNT electrodes are underway and initial results for the 17wt% composite cathodes are shown in Figure 6. These cathodes were cycled between 4.0 and 1.5V at a discharge rate of 560 mA/g and charge rate of 280 mA/g. The first and twentieth discharge curves are shown in Figure 6. These electrodes did not exhibit any capacity loss over the twenty cycles tested and delivered over 400 mAh/g per cycle. It is interesting to note that cycling data for similar vanadium oxide aerogel cathodes that used KJB as the conductive additive exhibited a significant capacity decline over twenty cycles with even slower discharge rates.⁴ In view of the excellent mechanical properties of carbon nanotubes, it is tempting to speculate that the SWNT's may actually reinforce the electrode structure, enhance its integrity and ensure that electrical contact is maintained throughout cycling. Future work is necessary to determine whether such mechanical effects do indeed influence cycling behavior.

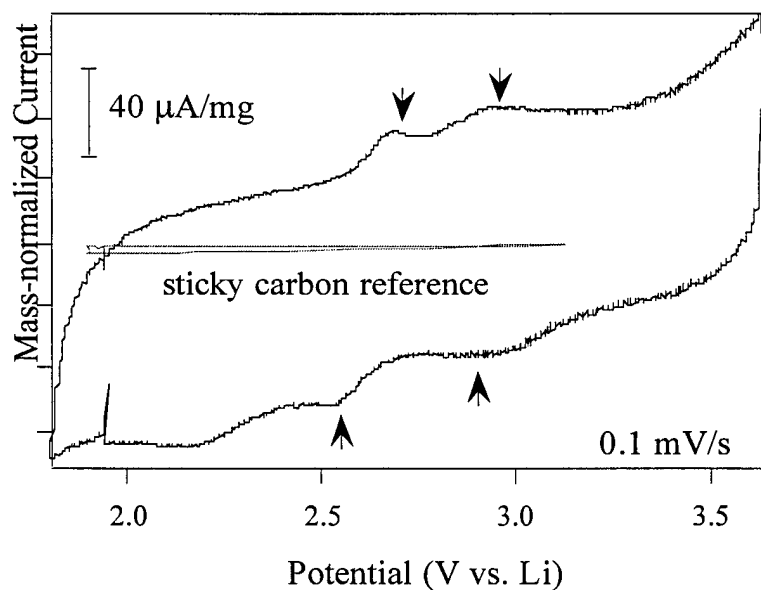
ACKNOWLEDGEMENTS

The authors are grateful for the support of their research by the Office of Naval Research.

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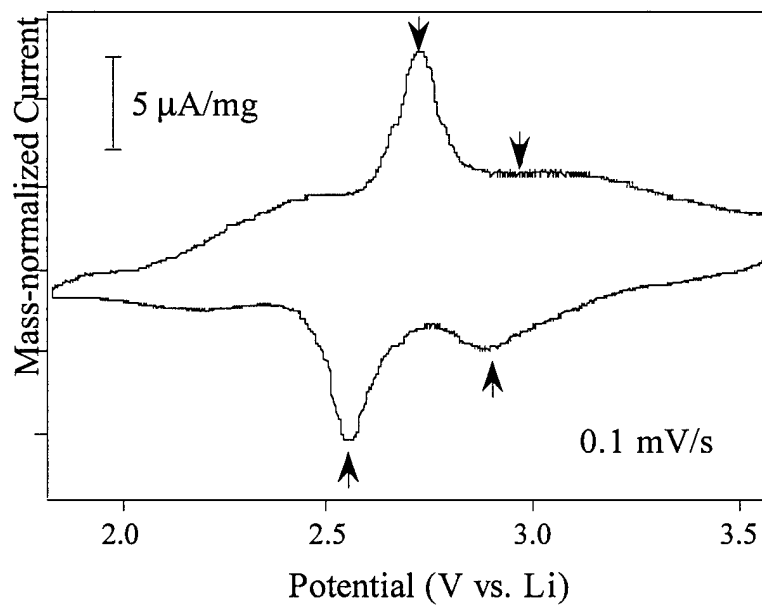


Figure 1. Voltammograms for scd V_2O_5 aerogels. (a) Sticky carbon electrode taken at a scan rate of 0.1 mV/s; (b) Conventional electrode consisting of the V_2O_5 aerogel, carbon black and PVDF taken at a scan rate of 0.1 mV/s. The electrolyte is 1.0 M $LiClO_4$ in PC. The arrows refer to the same voltages.

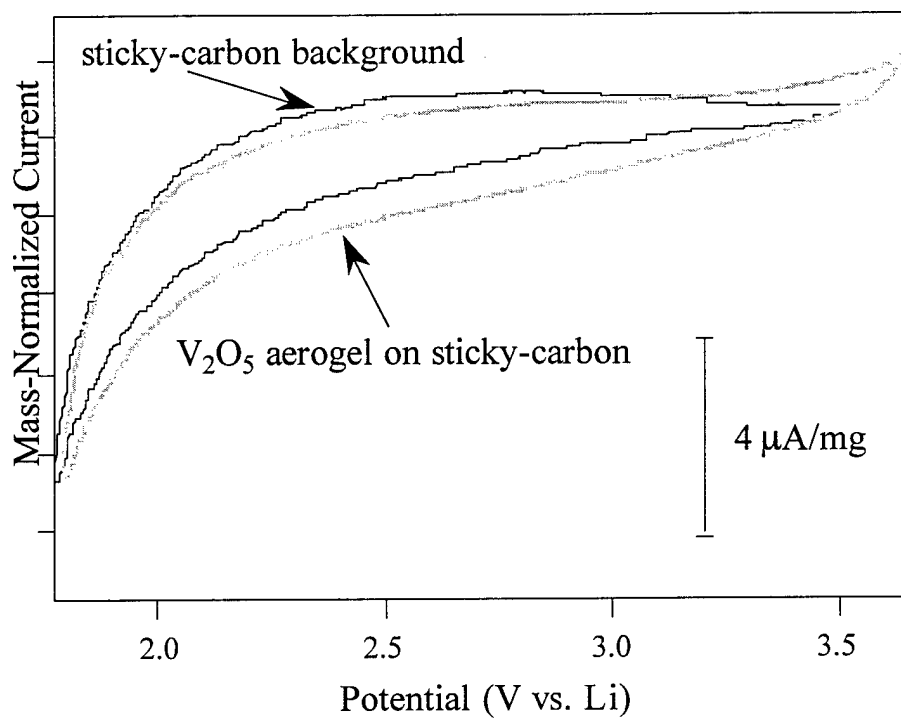


Figure 2. Voltammogram for sticky-carbon electrode and for V_2O_5 aerogel pressed on the sticky-carbon electrode. The data were taken at a scan rate of 0.1 mV/s. The electrolyte is 0.1 M TBAP in PC.

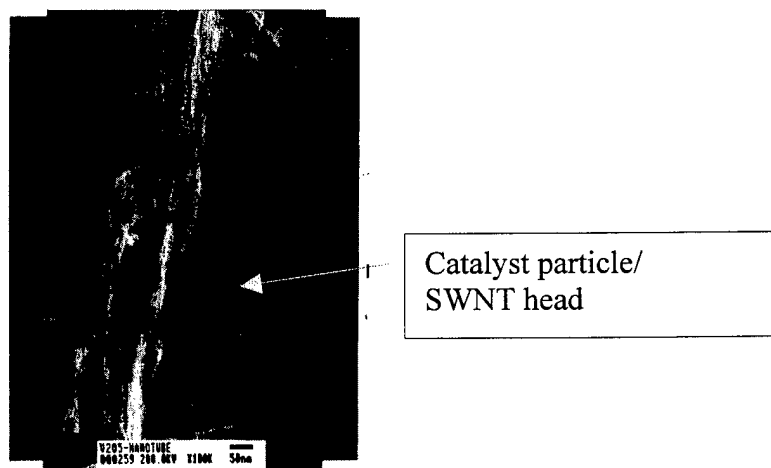


Figure 3. TEM image of the microstructure for the V_2O_5 aerogel - SWNT composite. The dimension bar is 50 nm.

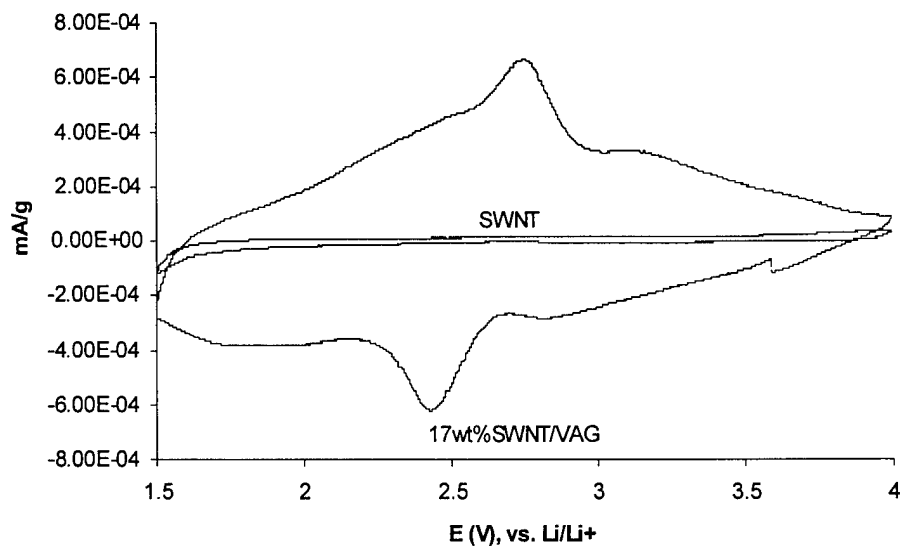


Figure 4. Voltammograms for SWNT and the V_2O_5 -SWNT (17 wt%) nanocomposite. The intercalation/deintercalation peaks for the nanocomposite are quite prominent. The voltammogram for the SWNT indicates that the carbon nanotubes do not contribute to the capacity of the composite electrode.

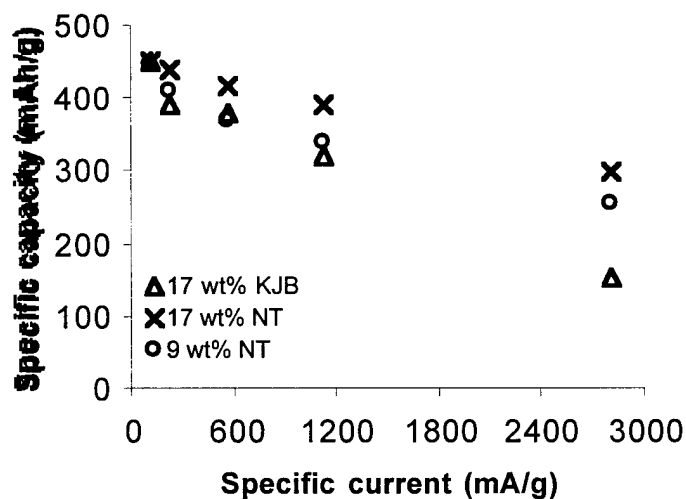


Figure 5. Specific capacity as a function of rate for V_2O_5 -SWNT nanocomposite electrodes with 9 and 17 wt% SWNT compared to a traditional electrode (V_2O_5 -KJB) which had an equivalent amount of conductive additive (17 wt%).

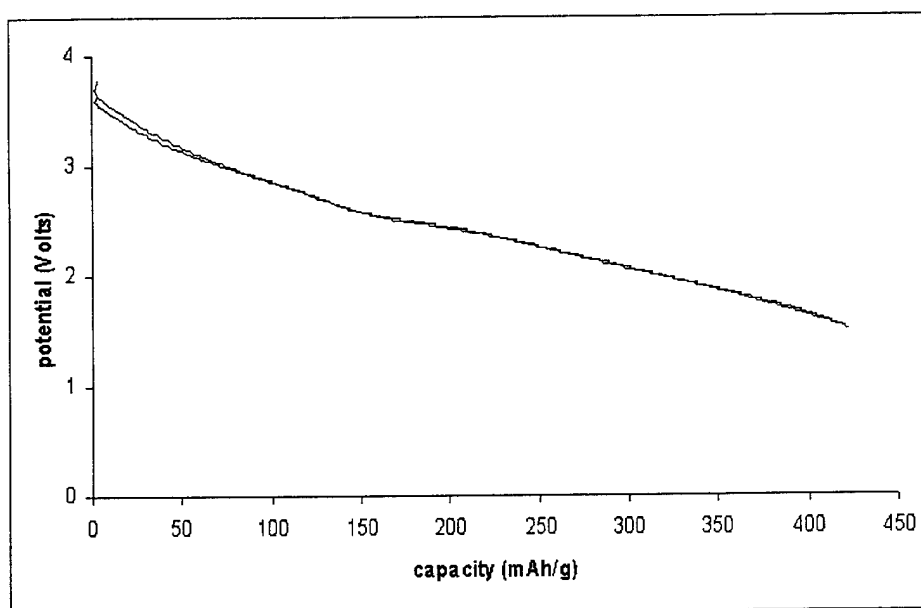


Figure 6. Discharge curves for V_2O_5 -SWNT nanocomposite electrode containing 17 wt% SWNT's. The first and twentieth discharge profiles are shown. No capacity loss is evident. The cells were cycled at 560 mA/g.